

Quantitative and Qualitative Prediction of Light Absorption by Colored Dissolved Organic Matter in the Coastal Zone

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LONG-TERM GOALS

To produce a physical water mass mixing model for describing colored dissolved organic matter (CDOM) distributions in the coastal zone. The model will combine the effects of local non-conservative processes with overall mixing of major CDOM end-members from terrigenous and marine sources. Although the model will be firstly derived for one study site (the entrance to the Baltic Sea) the approach will be designed for implementation in other regions of Navy interest (international estuaries and harbors).

OBJECTIVES

This project will provide a tool for predicting the quantitative and qualitative distributions of CDOM in the littoral zone based on combined model of CDOM biogeochemical cycling and physical oceanography. This approach provides the Navy with an alternative technique by which to gauge the performance of satellite based predictions of CDOM distributions. A major focus of this software will be the removal of CDOM “noise” in riverine and estuarine environments.

APPROACH

The study area is the Baltic Sea-North Sea mixing zone at the entrance to the Baltic Sea (Figure 1). The Baltic Sea is a large estuary greatly influenced by freshwater inflow from its large drainage basin ($1.63 \times 10^6 \text{ km}^2$) and limited exchange with the North Sea (Atlantic Ocean). As a result its waters have a high content of terrestrially derived organic material.

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Figure 1. Map of the Baltic sea indicating the countries that border it. The red square indicates the proposed study site; the Baltic-North Sea mixing zone.

The project has three work packages.

Work Package 1-Collection of a calibration data set

In order to achieve the goals of this project a comprehensive foundation of the seasonal variations in CDOM in these waters is needed. Although we already have a large degree of understanding of the processes controlling CDOM distributions in these waters (e.g. Højerslev et al 1996; Stedmon et al 2000), several contributing factors remain unknown. First, it is vital to have good seasonal coverage of CDOM variations in the region to accurately gauge the extent of this variability for these waters. The concentrations and characteristics of CDOM in the freshwater run-off varies with season (Stedmon and Markager 2005). Additionally, in spring and summer there is production of CDOM associated with phytoplankton productivity in the surface waters, although the importance of this source relative to terrestrial CDOM is currently not known.

The sampling strategy is coordinated with the Danish National Monitoring Program, which is based at NERI. NERI runs five cruises a year covering the whole study site (Figure 2). Originally the cruises were in February, August, September, and October. Now however due to national cut backs the October cruise has been cut. The February cruise is useful for studying the winter conditions where water mass mixing controls CDOM distribution. The summer to fall cruises will provide important information on the autochthonous production and degradation (photochemical and microbial) with time, of CDOM associated with summer phytoplankton productivity. (Responsible project partner: NERI, with some participation by NRL)

Measurements of the light absorption and fluorescence properties of CDOM will be made. Additionally recently developed detailed fluorescence spectroscopy techniques that characterize CDOM will be applied (Stedmon et al 2003). (Responsible project partner: NERI). Detailed chemical measurements will be used to describe the composition and hence source/extent of reprocessing of the organic material. These measurements will include carbon, nitrogen and phosphorus content

(DOC, DON and DOP), stable isotopic composition of DOM, and lignin content (Osburn et al 2001). DIC concentration and stable isotopic composition measurements will assist in water mass source provenance. (Responsible project partner: NRL).

This work package will provide insight to the underlying chemical compositional variations in CDOM leading to changes in its absorption spectra. Basic oceanographic parameters (temperature and salinity) and other water quality data (e.g. Secchi depth, diffuse attenuation, nutrient concentrations, chlorophyll) will be provided by the Danish, Swedish and German monitoring programs.

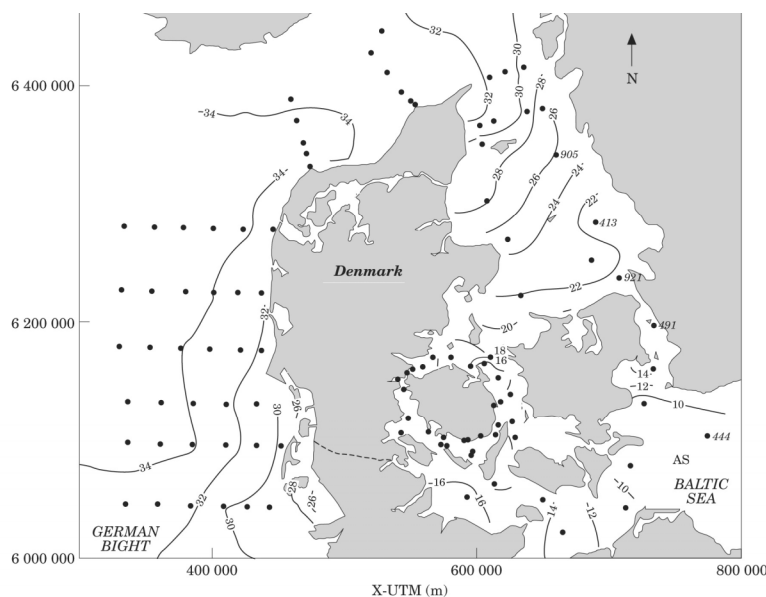


Figure 2. Close up of proposed study area at the entrance to the Baltic Sea. Refer to Figure 1 for location. Dots on the map indicate monitoring stations from the Danish National Monitoring program which will be used. Contour lines indicate the salinity gradient of the mixing zone between the freshwaters of the Baltic Sea to the East and the saline North Sea to the West. (Figure adapted from Stedmon et al 2000).

Work Package 2- Model adaptation and validation (Responsible project partner: NERI).

The current hydrodynamic model being implemented for the Baltic-North Sea region at NERI in Denmark is COHERENS. COHERENS is a 3-D hydrodynamic model for coastal and shelf seas developed over the period of 1990-1998 by a multinational European group, as part of the MAST projects funded by the European Union. Although the model includes other biological and sediment transport modules, in this project we will only be applying the physical modules for currents, salinity and temperature. At NERI this module is already set up and running for the Baltic Sea study region. The boundary conditions and atmospheric forcing data for the model are collected and freely available to the project.

The goal of this work package will be to validate the model by comparing the predicted results against the collected data from the monitoring cruises. Once we are satisfied with the models description of the

physical water mixing occurring we can proceed with integrating the CDOM optical properties into it (Work Package 3).

Work Package 3- Integration (Responsible project partner: NERI).

The final phase of the project will involve the integration of the physical mixing model with our understanding of CDOM properties in these waters. Some initial studies suggest that despite the fact that DOM is a very dynamic component of several biogeochemical cycles, much of its variability in quantity and quality can be explained by conservative mixing (Højerslev et al 1996; Stedmon & Markager 2003; Hansel et al 2004). This is especially true for the months of the year outside of the phytoplankton growth season. During the spring bloom and summer bloom a significant amount of autochthonous CDOM is produced and adds to the background allochthonous signal. Recent work in Polish coastal waters has revealed that these deviations from conservative behavior can easily be modeled (accounted for) by including simple empirically derived models of biological production of CDOM (Kowalczyk et al 2006). A similar approach will be applied in this project. Firstly the properties of the CDOM end members in the mixing zone will be described and placed into the physical mixing model. Model prediction of CDOM distributions and characteristics will then be compared with measured values from WP1 and the degree of conservative mixing assessed. This will allow us to secondly evaluate the scale of impact of the non conservative processes (photochemistry and biological production) and hereafter include them when necessary using a multi-linear regression approach.

WORK COMPLETED

The project officially started in April 2006. Project planning meetings have been held at NERI in June 2006 and February 2007.

Work Package 1: To date six cruises have been completed and the samples from the first four are analyzed and the data is worked up. Each cruise consists of approximately 25 stations and 200 samples.

Work Package 2: The project is currently working in collaboration with the modeling group at NERI and evaluating different approaches for implementing CDOM into the existing COHERENS model for the region. These solutions range from simple empirical salinity relationships to more complex bio optical modeling.

Work Package 3: Initial analysis on the relationships between water mass mixing (salinity) and phytoplankton (chlorophyll) is underway (see below). With the first years data collected and worked up, models can now be developed and tested on the data currently being collected (August, September 2007 and February 2008).

RESULTS

The initial CDOM absorption data from the first four cruises is shown in Figure 3. Here it is clear that a large fraction of the variability in CDOM in these waters is explained by the mixing of the brackish Baltic Sea water rich in CDOM with the more saline North Sea water with lower CDOM concentrations. There appears to be two mixing gradients; a) across the salinity range of 8 to 31 representing the Baltic outflow and b) over the salinity range of 32-35 representing the mixing of a

Baltic Sea/North Sea coastal intermediate water mass with offshore North Sea water. Initial analyses reveal that both mixing lines can be modeled reasonably well with linear models indicating that much of the CDOM in the region mixes conservatively. However there is a degree of deviation from conservative mixing, in particular in August between salinities of 8 and 31 (Figure 4). Several points fall below the mixing line. The deviation is most likely a result of both autochthonous production of CDOM and photochemical removal of CDOM in surface waters during summer. Initial regression analysis results reveal that a model with salinity and chlorophyll can account for 89% of the variability in CDOMs a_{300} in August (Figure 5a). However a collection of data points in the salinity range of 17-23 deviate notably from the model with lower a_{300} values. These originate from surface water samples (1 and 5m depth) in the Central and Northern Kattegat and it is thought that photodegradation is responsible. CDOM spectral slope (S) values for these samples are also higher than for the other samples which agrees with the photodegradation hypothesis. Similar analyses are now being carried out on the other cruise data with the aim of deriving a set of robust empirical relationships which can be easily implemented in the regional hydrodynamic models.

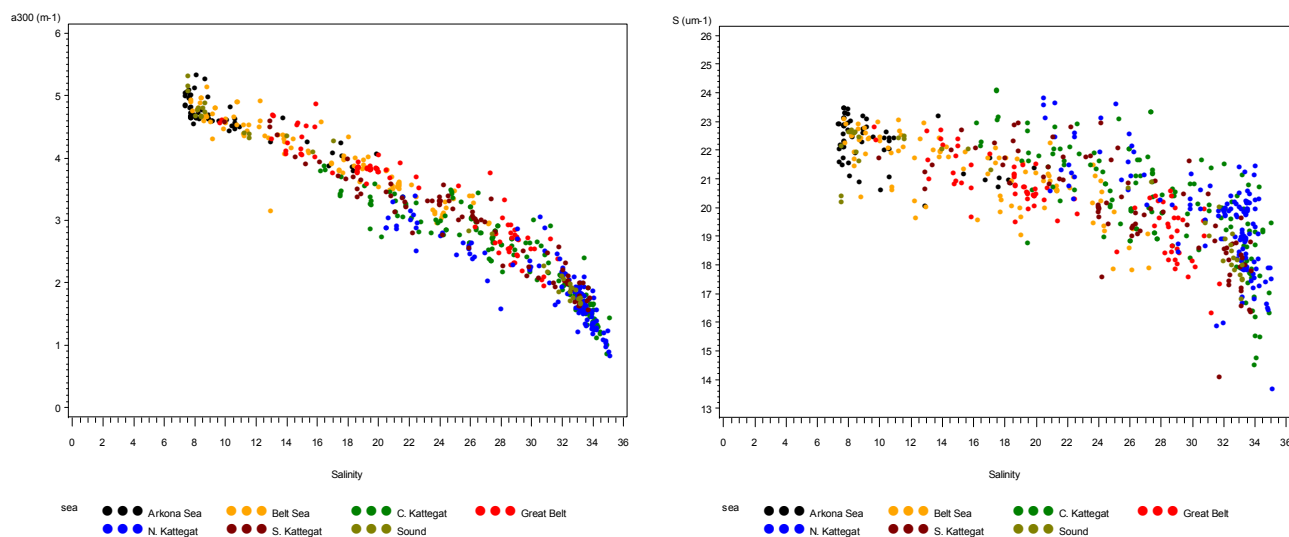


Figure 3. Results of the CDOM measurements taken from the last 4 cruises. On the left hand side CDOMs absorption at 300 nm (a_{300}) is plotted against salinity. There is a general linear decrease in a_{300} with increasing salinity, revealing the quasi-conservative behavior of CDOM in these waters. On the right hand side CDOMs spectral slope is plotted against salinity. In general there is a gradual decrease in S with increasing salinity.

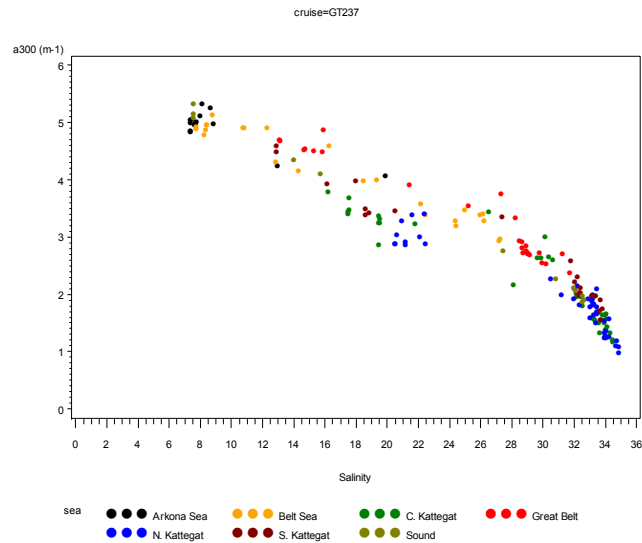


Figure 4. CDOM a_{300} in August 2006 plotted against salinity. The data show that there is a degree of deviation from the linear mixing line. In particular sample from the surface waters of the Kattegat appear to lie below the general mixing trend.

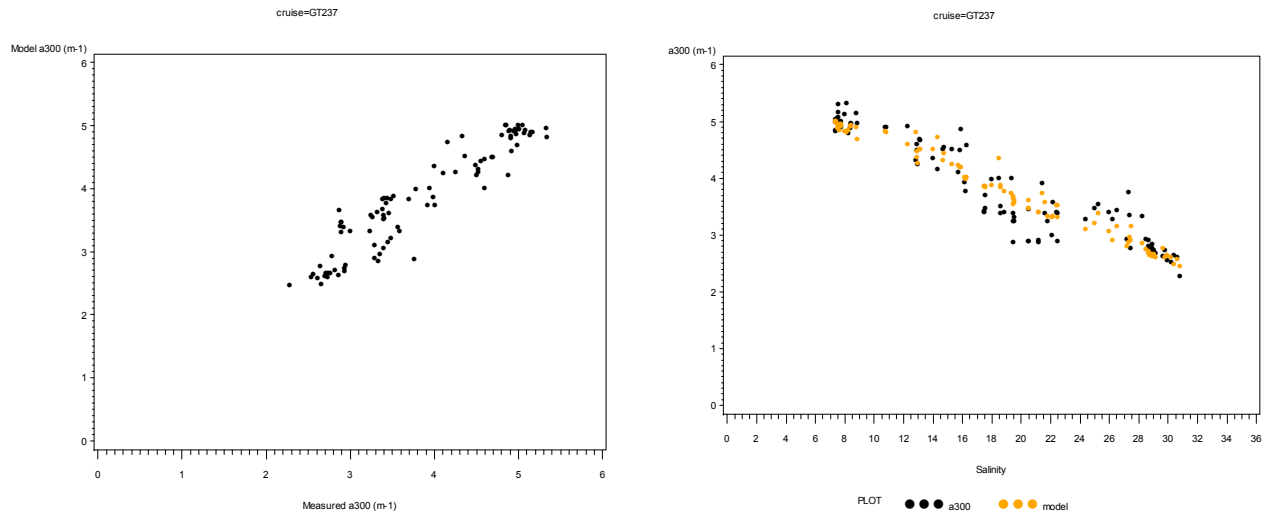


Figure 5. Results of initial regression analysis between CDOM a_{300} and salinity and chlorophyll for the August 2006 data ($r^2=0.89$). The left hand graph shows the predicted a_{300} against the measured a_{300} . The right hand graph shows the measured and modeled a_{300} plotted against salinity.

IMPACT/APPLICATIONS

The project area is relevant to the three major interest areas of the Ocean, Atmosphere and Space department (Code 32) at ONR: Battlespace Environments, Anti-Submarine Warfare and Mine Warfare. These three science and technology areas all have a vested interest in underwater optics in the coastal zone. The success of future development and increased application of airborne, satellite and sub-

marine optical sensors in these waters is largely dependent on removing the CDOM signal. Dynamical physical mixing models are already used in a wide range of oceanographic research and monitoring applications, however the use of these for predicting CDOM distributions is not widespread. The proposed biophysical model would generate forecasting and nowcasting data to support the Navy's Littoral Remote Sensing program and FNC Littoral Antisubmarine Warfare as a major improvement in information awareness and characterization of the littoral battlespace, especially in terms of the inherent optical properties (IOPs) of water, or "water clarity." Data and/or forecasts of IOPs, for example, are useful to mission planners needing to predict diver visibility undersea in addition to the efficacy of laser- and camera-based detection systems under variable conditions in the littoral zone.

Finally this project will provide scientists with an improved understanding of CDOMs influence on the underwater light climate in these waters. Current ecological models do not take into account CDOMs effect on light attenuation and hence are not able to reproduce the correct photic depth, leading to elevated areal primary productivity estimates. With increased knowledge of the variability of CDOM and the integration of empirical models derived from this project a better estimation of the photic zone can be made in the models.

RELATED PROJECTS

There is a high degree of synergy between this project and another project held by C. Stedmon funded by the Danish Technical Science Research Council. The project is focused on improving fluorescence characterization methods for CDOM and providing increased insight on the correlations between its chemical and optical properties. Project started in 2005 and ends in 2007, with a budget of 1.4 million DKK (approx. US\$230,000).

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